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Magnetic Surfactants

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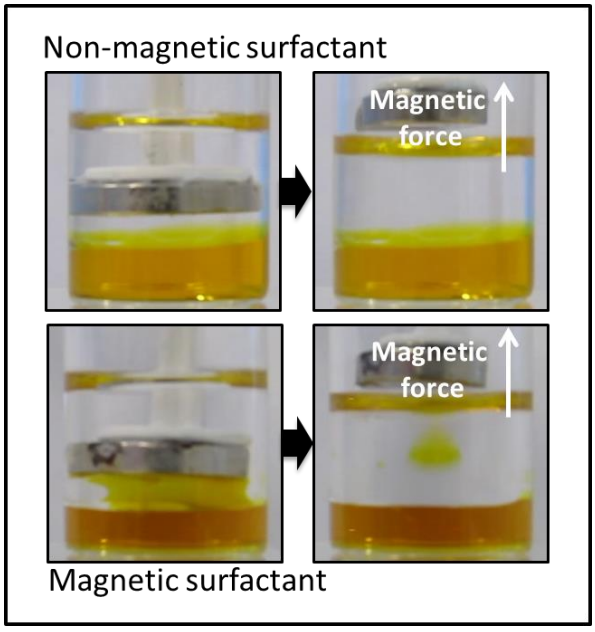
Abstract

Surfactants are ubiquitous, being important commodity chemicals with wide industrial applications, and essential components of living organisms. By generating stimuli responsive surfactants self-assembly and physicochemical properties of a wide variety of materials may be readily manipulated, both reversibly and irreversibly. Until recently magnetically-responsive surfactants had not been reported. This review reports the recent progress in magnetoresponsive surfactants, covering control or interfaces and bulk solution properties. The use of these magneto-surfactants as novel molecular magnets is also investigated as well as looking forward to potential applications.

Graphical Abstract



Highlights

- Introduce the 3 existing classes of magnetic surfactants; ionic, coordinating, covalently bound
- Consider a potential 4th class of magnetic surfactant
- Describe how these surfactants function as molecular magnets
- Report potential applications ranging biochemistry to water treatment
- Discuss the origins of magnetism in dilute aqueous solutions

Keywords

Stimuli responsive surfactants, molecular magnets, magnetic ionic liquids, chelated surfactants, polyoxometalates (POMs).

1. Introduction

Surfactants adsorb preferentially at interfaces and decrease the surface or interfacial tension between bulk media: the term surfactant is a portmanteau of "surface active agent". The molecules adsorb as they are amphiphilic – that is, they have one part containing a solvophobic "tail" and another containing a solvophilic "head". For this reason they are employed extensively as detergents, wetting agents and emulsifiers, and for enhancing the solubilization of a variety of chemical species either by dissociating aggregates or unfolding proteins [1, 2]. In addition, they also generate self-assembly structures in solution over nanometer to micron length scales such as micelles, microemulsions, emulsions and liquid crystals, affecting physicochemical and optoelectronic properties [3]. The ability to tune self-assembly in a predictive way introduces the concept of compartmentalization and structuring for control in phase-transfer catalysis [4].

Conventionally, self-assembly is manipulated either by varying pH or ionic strength, leading to irreversible changes in system composition, structure, or phase behavior, or by varying temperature, requiring significant energy input. A more sophisticated approach is to use external stimuli to activate reversible changes in molecular structures with responsive surfactants [5]. This has been achieved through sensitivity towards changes in CO_2 levels [6], light [7], enzymes [8] and electrical potential (redox) [9]. Interestingly, many of the

redox-active surfactants would also be expected to be paramagnetic. For example, Ru-based polyoxometalate (POM) surfactants convert between low-spin d^6 and high-spin d^5 through electrochemical activity [10], and oxidized ferrocenyl-based surfactants contain high spin d^6 paramagnetic centres [11]. Similarly, metallosurfactants containing *d*- or *f*- block metals as integral structural components had also received attention as a means of facilitating catalytic activity at interfaces and templating mesoporous materials [12]. However, in all cases their intrinsic magnetic sensitivity was largely overlooked. Recently, while investigating magnetic ionic liquid surfactants (MILSs) [13] it was noticed that even dilute aqueous solutions retained a magnetic response and that now surface tension could be modulated in a magnetic field [14, 15]. This discovery adds to the armory of responsive stimuli allowing for surfactant properties to be controlled simply by the switching "on" and "off" of a magnetic field. This review looks at three classes of magnetic surfactants, i) ionic surfactants whereby an electrostatic interaction exists between the metal counterion and surfactant head group, ii) coordinating surfactants, where the metal ion is chelated to the surfactant head group, and iii) covalently bound surfactants, where the metal is covalently bound to the surfactant head group, and also explores the potential of iv) purely organic magnetic surfactants formed from radicals. The origin of magnetism in these systems is considered, as well as exciting recent applications of these intriguing surfactants.

2. Magnetic ionic liquid surfactants – Class 1

Ionic liquids (ILs) are routinely considered to be salts with a melting point below and arbitrary 100 ^{o}C [16]. Though, a more accurate definition might be to call them molten salts containing organic moieties. They exhibit interesting properties such as low vapour pressures, high thermal stability, large electrochemical windows, and have unique solvent properties which are proving useful for many separation processes [16]. ILs containing transition metals had been known for some time [17, 18] but it had always been assumed that the metallic centers were isolated, lacking long-range interactions and communication necessary to be magnetically active [19]. Hayashi *et al*. reported in 2004 that 1-butyl-3-methyl-imidazolium tetrachloroferrate, [bmim][FeCl4] did in fact exhibit magnetic properties under the application of a small magnet (0.55 Tesla) [20]. Subsequently, after experimental confirmation that [emim][$FeCl_4$] showed 3-dimensional ordering below 4K, magnetic

interactions were reconsidered [21]. More recently, García-Saiz *et al*. showed that superexchange coupling could occur via two diamagnetic intermediaries [19].

In the past 10 years a large variety of magnetic ionic liquids (MILs) have been generated with iron, cobalt and gadolinium containing anions [22]. The interest arises from the fact that they are molecular liquids, rather than typical ferrofluids which comprise magnetic colloidal particles (≥10 nm) dispersed in a carrier fluid [23]. The nanoparticle-free MILs are themselves paramagnetic and have opened up many new research areas of interest including fluid-fluid separations and chemical reactions [24]. Because MILs are non-volatile they offer advantages over conventional ferrofluids which often employ flammable organic solvents.

By increasing the alkyl chain length of the imidazolium moeity to C_{10}, it was demonstrated that the ionic liquid 1-methyl-trimethylimidazolium tetrachloroferrate (C_{10}mimF) is surface active to generate a magnetic ionic liquid surfactant (MILS) [14, 15]. The authors then made more MILSs through the metathesis of common cationic surfactants with ferric chloride. Interestingly, at the air-water interface, in the absence of an applied magnetic field, the magnetoresponsive surfactants are more effective than a magnetically inert analogue (Figure 1), showing greater surface tension (γ) reduction of water for the same concentration. On placing a magnet (0.4 T) close to the aqueous solutions the magnetoresponsive surfactant reduces γ even further.

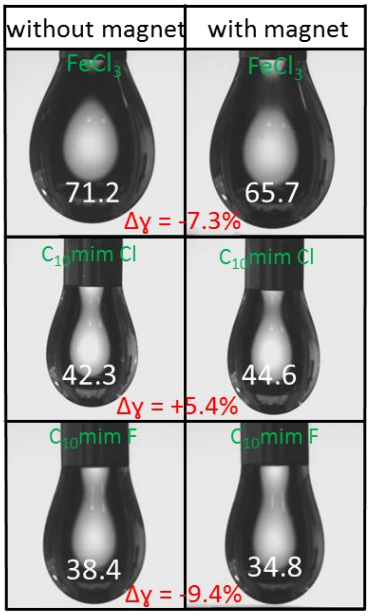


Figure 1: Response of liquid droplets to the field from a 0.4 T NdFeB magnet. [C_{10}mimCl] and [C_{10}mimF] =20 wt % [14].

For surfactants based on Ho and Gd even greater responses were observed, though now the compounds were no longer ionic liquid in nature [15]. It should be noted that these measurements were not quantitative. The pendant drop method used by the authors estimates the surface tensions from the Young-Laplace equation [25]:

$$\Delta P = \gamma(\frac{1}{R_1} + \frac{1}{R_2})$$

where ΔP is the pressure difference across the fluid interface, and R_1 and R_2 are the radii of curvature. Here, the equilibrium drop shape is a result of competition between gravity, which tends to detach the drop and surface tension which keeps the drop connected to the tip. The magnetic field is responsible for an extra force, acting on and deforming the drop, and increases as a function of the fraction of magnetic material. For conventional ferrofluids estimates of γ in a magnetic field have been achieved by modification of the aforementioned equation with those of Maxwell [26]. For the case of the MILSs in aqueous solution, further studies are required.

Degen *et al*. recently used X-ray reflectivity (XRR) to provide insights into Fe accumulation at the interface for a 1-dodecyltrimethylammonium trichloromonobromoferrate (DTAF) [27]. They reported an extremely small layer thickness, as is typical of conventional surfactants, and suggested that this was not enough for paramagnetic response to occur from just surface iron ions. Without doubt, bulk material plays a role in the "apparent surface tension" reduction of these materials, however, there was no report on interfacial structuring under the influence of a magnetic field. In particular dissociation effects of the cation-anion pairs must be considered. If the Fe ions are pulled from the bulk to the surface due to the magnetic force then a percentage of surfactant anion should be expected to be pulled along to retain electrostatic neutrality. This should not be underestimated, as throughout this review it will hopefully become clear that, even though the mechanism is poorly understood, even very low levels of surfactant, all of which are adsorbed at an interface (e.g. graphene-water, protein-water, *etc.*), can elicit dramatic responses in magnetic fields without the need for bulk material. This may also be the case for the surfactant iron chloride mixtures the authors studied too, as, perhaps unexpectedly, ferric ions interact even with non-ionic surfactants such as Brij making them magnetic [28]. The

important distinction is that the MILSs consist of a one component systems and also may allow for new extraction techniques as, for example, it may be possible to undertake a reaction in a surfactant mesophase and then concentrate the solution ready for extraction in an magnetic ionic liquid phase in a way not available to simple surfactant + $FeCl_3$ mixtures.

2.1 Structuring of MILSs and magnetic properties

It was demonstrated that these new MILSs behaved like conventional surfactants in that they form micelles and various lyotropic mesophases above a critical micelle concentration (cmc) [14, 15]. It was attempted to measure the cmc as a function of effective magnetic moment (determined by vibrating sample magnetometer) for a holmium based surfactant [15]. It was hypothesized that this may look similar to a conductivity versus concentration plot [29], where a change in the gradient may be observed at the cmc due to the partitioning of metal centres near each other once aggregation occurs. The cmc was determined by electrical conductivity and corroborated by SANS (both 31 mM). The corrected magnetization graphs for all concentrations showed straight lines with no sign of hysteresis (Figure 2). The most probable reason that no transition was observable is that the magnetic counterions in these systems are weakly dissociated around the micelles and also due to thermal fluctuations.

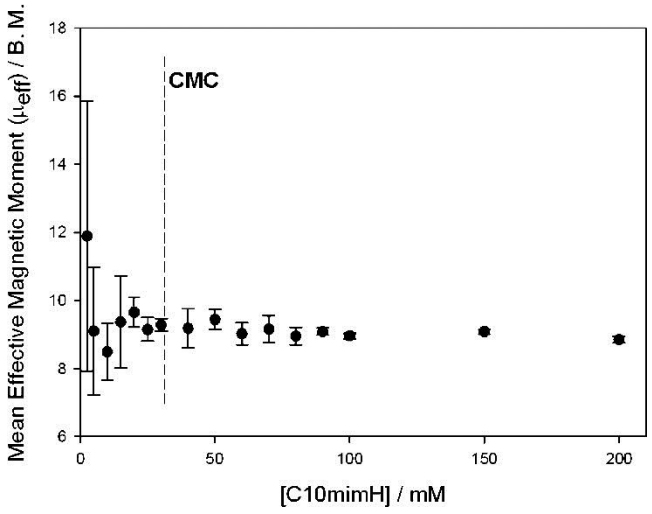


Figure 2: The relationship between the mean effective magnetic moment μ_{eff} and the concentration of magnetic surfactant 1-decyl-3-methyl-imidazolium tetrachlorogadolinate (C_{10}mimH) [15]. Reprinted with permission from Langmuir, 2013, 29 (10), 3246-3251. Copyright 2014 American Chemical Society.

This is in complete contrast to some water-in-oil microemulsions (inverse micelles) that were studied, where, although dissociated, the counterions are partitioned into the small volume of the aqueous droplets and are in close proximity to one another [30]. The authors demonstrated that the Ho-based microemulsions were ferromagnetic below 75 K but superparamagnetic above that temperature, which was in contrast to the magnetic phase behavior of the pure surfactant (paramagnetic down to 5 K). This may be compared to magnetite nanoparticle-based Pickering emulsions [31]. In this case dry samples were ferromagnetic but colloidal samples were superparamagnetic. One explanation could be that there is a magnetization reorientation barrier due to magnetic anisotropy, whereby random fluctuations are suppressed. For magnetic nanoparticles a contribution from both the bulk material (magnetocrystalline anisotropy) and the surface anisotropy is observed. However on reducing the domain size on the formation of microemulsions (typically n = 75–150) or micelles (n ~20) the magnetic moments of the clusters become sensitive to thermal fluctuations, with individual atomic moments maintaining their ordered state relative to each other (high domain alignment) as only surface anisotropy is displayed. These systems may now provide an intermediate between MNPs and molecular magnets [32].

At this point it is interesting to compare work completed by Gadzielski *et al*. who generated magnetic IL-in-oil microemulsions [33]. The authors demonstrated a macroscopic effect (pulling the bulk material along a field gradient), though control of individual nanodomains was not reported. Hatton *et al*. used SANS in a magnetic field (1.6 T) to ascertain if such control was possible [34, *c.f. Supporting Information*]. Almost no variation between the profiles was detected due to the effect of a magnetic field (Figure 3), though the difference was actually measurable and within error. A subtraction of the 0 T data from the 1.6 T data exemplifies this. The small difference may be a result of the ionic liquid effect but could potentially just be a result of changes in molecular bonding and van der Waals interactions in such a high field. There is perhaps justification to repeat these experiments at cryogenic temperatures where thermal fluctuations (k_BT) are small and also to investigate transition temperatures and other magnetic behavior using a range of techniques from polarized neutrons to AC and DC SQUID magnetometry. In this respect they stand as ideal model systems to investigate magnetic response of MILSs in soft matter systems.

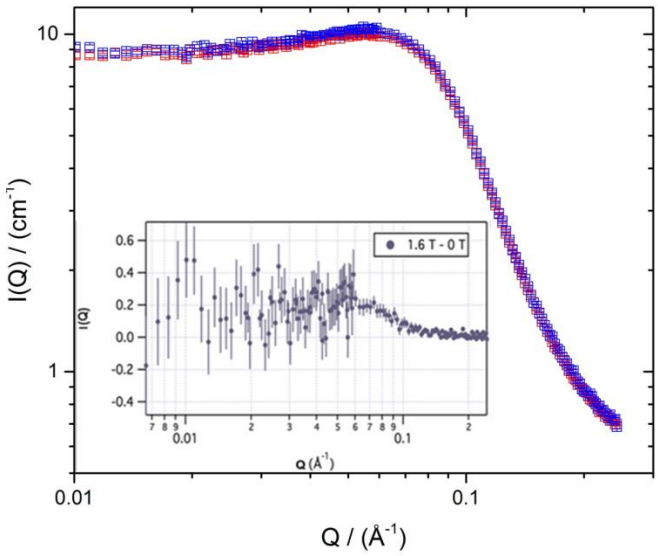


Figure 3: SANS profiles of magnetic microemulsion in the absence of a magnetic field (blue squares) and in the presence of a 1.6 T homogeneous magnetic field (red squares).Error bars smaller than plot symbol; **(inset)** The subtraction of the SANS profile at 0 T from the profile taken in a field of 1.6 T. Error bars represent standard deviations derived from neutron counts [34]. Reprinted with permission from Langmuir, 2014, 30 (15), 4267-4272. Copyright 2014 American Chemical Society.

2.2 Control of Emulsions

Like microemulsions, emulsions are mixtures of two or more immiscible liquids stabilized by interfacial adsorption of surfactants or particles [34]. Unlike microemulsions, emulsions are not thermodynamically stable but they usually require a much lower mass fraction of surfactant for generation [34]. As such they are essential components in many processes and products, such as pharmaceutical, agrochemical formulations, paints, oil recovery and foods [34]. Previously, magneto-responsive emulsions had only been realized with Pickering emulsions, stabilized by pre-synthesized magnetic nanoparticles, and this limits scale-up applications [36]. By employing Gd- and Fe-based magnetic surfactants the authors could generate emulsions using brine and commercial lubricant oil, demonstrating how they may be prepared and implemented for practical applications [37]. Emulsions could be “levitated” through the air using strong magnets and also were prepared to “flow” through a tube under the influence of a 0.37 T magnet. It has been reported that a magnetic field strength of 0.2-0.7 T is needed to efficiently capture particles and control emulsions flowing in blood vessels, indicating the

suitability of these systems for nanomedical applications (Figure 4). Such emulsions may also function as treatment fluids for use in a variety of subterranean operations for increasing viscosity or temporarily separating different portions of fluid systems [38].

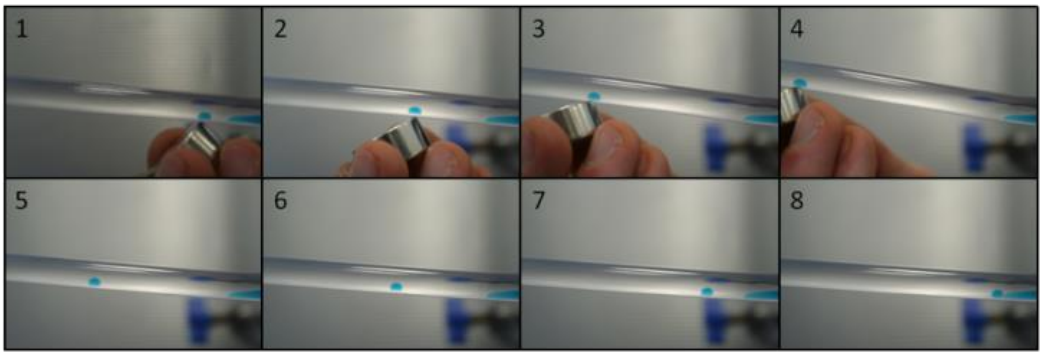


Figure 4: Effect of a magnetic field (0.37 T) on a DTAG based emulsion droplet (dyed with methylene blue for visualization) in a dodecane background. DTAG (50 wt%) oil (dodecane, 10 wt%). The droplet is pulled against gravity and viscosity of the dodecane fluid (picture 1–4). Once the magnet is removed (picture 5) gravity causes the droplet to flow back down the tube. Reproduced from Ref. [37] with permission from The Royal Society of Chemistry.

2.3 Control and Manipulation of Biomolecules

In the field of biotechnology, the effective control over the transport and delivery of biomolecules is still a major challenge but is vital for protein separations [39], the regulation of gene suppression and targeted drug delivery [40]. Again, heterogeneous dispersions of magnetic nanoparticles have provided most of the solutions and been used with some success [41, 42]. However, there are often many drawbacks to their efficient employment such as bioreactivity, toxicity, and sedimentation [43]. In addition the synthesis of ultrafine particles can also be challenging and the ensuing interactions between the particle surface and the biomolecules may disrupt native form and function. Using magnetic surfactants could offer significant advantages in this respect, due to facile synthesis, effective binding and good dispersibility in solution.

DNA readily binds to cationic surfactants and leads to effective compaction. This is crucial for gene therapy and protecting DNA from nuclease and allowing endocytosis. It has been demonstrated that magnetic surfactants based on Gd, Ho, and Fe anions and a dodecyltrimethylammonium cation (DTAG, DTAH, DTAF respectively)

could compact herring sperm DNA to a greater extent than the non-magnetic analogues without disrupting helical structure (Figure 5) [44]. Importantly, it was shown shown that low strength magnetic fields could be applied to induce aggregation and concentrate DNA in very dilute solutions (150 μM DNA, 50 μM DTAG). The fact that the surfactants exhibit a magnetic response at such low concentrations is fundamentally important. It is an interesting question as to whether the assembly of surfactant at the biomolecule/water interface is what causes the remarkable response, in a similar fashion to microemulsion systems described above.

Using atomic force microscopy (AFM) Xu *et al*. demonstrated that not only do DNA-magnetic surfactant complexes migrate in a magnetic field but that compaction also occurs (Figure 5) [45]. After 48 hours they saw an 80% reduction in size simply by the presence of a magnetic field. The novelty of their work is that they incorporated a light-responsive moiety into the surfactant to create the dual-responsive surfactant 4-ethoxy-4'-(trimethyl-aminoethoxy) azobenzene trichloromonobromoferrate (azoTAFe) which then allowed for the reversible decompaction of the DNA on impinging the solution with UV or visible light. The authors concluded that the dual response of their surfactant led to greater compaction of DNA and occurred at much lower surfactant concentrations.

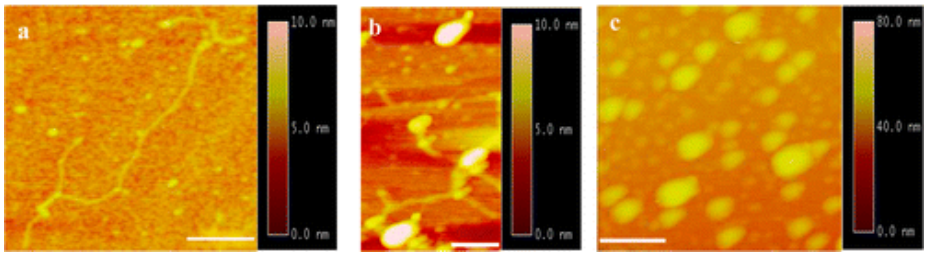


Figure 5: (a) AFM image of stretched DNA/azoTAFe complex coexisting with 0.01 mmol L^{-1} azoTAFe micelles without a magnet; **(b)** Coexisting coil-globular state of DNA with 0.01 mmol L^{-1} azoTAFe after the introduction of a magnet (0.25 T) for 24 h; **(c)** Completely globular compacted DNA with 0.01 mmol L^{-1} azoTAFe after being in a magnetic field for 48 h. Scale bar is equal to 100 nm [45]. Reprinted with permission from ACS Appl. Mater. Interfaces, DOI: 10.1021//acsami.5b01514. Copyright 2015 American Chemical Society.

Magnetic induced migration using surfactants has also extended to model proteins such as myglobin and green fluorescent protein (GFP). Although it is known that cationic surfactants can denature myglobin via strong binding adding DTAH below the cmc did not change the positions of the characteristic adsorption bands, suggesting preservation of tertiary structure. This finding formed the basis of investigations of separation and purification of proteins [46]. Gd based surfactants and the homopolymer poly(3-acrylamidopropyl)trimethylammonium tetrachlorogadolinate were employed as a new family of magnetic nanocarriers. Conventionally, it is the corona of proteins adsorbed onto magnetic particles that act as the carrier-cell interface and determines nanocarrier performance. However, in the case of this work it was the corona of the adsorbed surfactants and polymer which acted as the interface. It was demonstrated that the surfactants and polymers had different affinities for various proteins in a solution of fetal bovine serum (FBS) The surfactant-protein complexes could be rapidly (5 minutes) separated from unbound proteins and cell debris resulting in purified proteins. Gel electrophoresis showed strong bands corresponding to proteins of 63-75 kDa, attributed to fetuin and other albumins (Figure 6). Fetuin enhances cell growth by facilitating cell attachment by inhibition of proteolytic activity. Therefore, it is becoming increasingly studied and this method of rapid purification is becoming of interest [47]. The authors also showed the biocompatibility of these new magnetic materials was almost as good as their non-magnetic analogues, and in the case of $Gd(AOT)_3$, better.

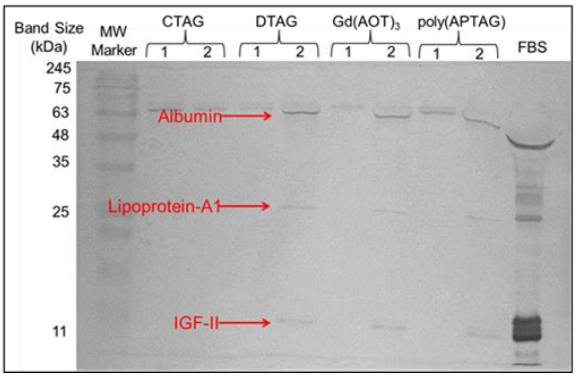


Figure 6: Bands in electrophoresis gel after silver staining. Samples numbers refer to two methods used [46].

We mentioned earlier some of the drawbacks of using nanoparticles but there are also many advantages. For example, gold nanoparticles can exhibit surface plasmon resonance [48], high specific areas, good biocompatibility and easy surface modification [49]. However, there is a dearth of reports pertaining to their targeted transport because they are diamagnetic. Attempts to alter their magnetic behavior usually involve preparing "core-shell" structures, which lose many of the gold nanoparticles' unique properties and also lead to a loss of biocompatibility [50]. Xu *et al*. developed a protocol for preparing magnetic gold nanoparticles via one-step modification with a paramagnetic cationic surfactant [51]. The resultant magnetic particles were able to bind to and manipulate DNA and proteins in a low strength magnetic field while retaining the benefits of using colloidal gold.

Finally, it is worth mentioning the recent study by Anderson *et al*. who reported the use of hydrophobic MILs for the rapid extraction (~60%) of double stranded DNA from aqueous solution [52] circumventing the need for time consuming centrifugation steps. The authors claim the extracted DNA was in sufficient quantity and quality for polymerase chain reaction (PCR) amplification, which might find application for downstream analysis. The MILs used were not surface active and it may be of interest to consider the dual capabilities of a magnetic ionic liquid surfactant whereby compaction of DNA via surfactant properties is combined with efficient extraction due to the ionic liquid nature. Recent efforts to tune the hydrophobicity of MILSs have recently been reported [13, 53].

2.4 Adsorption on Inorganic Surfaces

Graphene oxide (GO) sheets were first synthesized over a century ago and are the "liquid phase oxidation-exfoliation product of graphite" [54]. They readily form stable colloidal dispersions in water as some of the sp2 hybridized carbons atoms are derivatized by epoxide and phenol hydroxyl groups. Unoxidized hydrophobic domains do still exist turning GO into a surfactant sheet, capable of lowering interfacial energies [55]. They have attracted a great deal of interest over the past decade with potential in multifarious applications ranging spectroscopic sensors [56], battery electrodes [57], and more recently water treatment [58, 59]. The large surface area to mass ratio combined with unique surface properties has led to investigations into their use as

adsorbent material for the removal of toxins from aquatic environments. However, for application realization, efficient recovery post-sorption is required. Covalently binding GO to magnetic nanoparticles has been attempted but requires high energy, complex and multistep synthetic procedures and effects adsorption capacity of the sheets [60, 61]. Tabor *et al*. used magnetic surfactants (DTAF) to bind to the GO (at pH 5.5 to ensure GO had a negative charge) [62]. The surfactant was reported to bind with moderate affinity, leading to significant flocculation. These DTAF-GO flocs could then be controlled by a magnetic field. The authors raise an interesting point about the binding properties of the surfactants and the nature of magnetic response. They consider the fractional level of counterion dissociation to be a key parameter and suggest that some undissociated surfactants binds to the GO and respond to the magnetic field, while other, dissociated surfactants retain their counterion in a diffuse layer near the surfactant-GO interface and that "by magnetic movement of the dissociated counterions, the surfactant-GO complex is osmotically "dragged" with them". The authors demonstrated that GO could successfully be used to separate traditionally difficult-to-recover gold nanoparticles from water, by using nanoparticles adsorbed onto the surface. Sadly, the same experiment was not repeated using the magnetic surfactants but it does illuminate potentially advantageous methodologies in decontamination.

Magnetic surfactants also adsorb onto other inorganic material such as silica, allowing them to be dispersed in organic solvents (organosols) [63]. The surfactants also cause the silica to become charged in nonpolar solvents, with research intensifying due to the development of electrophoretic displays, which are used to form electronic paper screens [64]. By using a holmium analogue of a common di-chain surfactant didodecyldimethylammonium bromide (DDAB) it was shown that the resulting nanoparticles had electrophoretic mobilities three times larger than the analogous non-magnetic systems (-5.9×10^{-10} m^2 V^{-1} s^{-1} and -17.6 10^{-10} m^2 V^{-1} s^{-1} respectively) and importantly they now also demonstrated magnetophoretic mobility. The authors demonstrated control of particles in a magnetic field using turbidity measurements with sedimentation and redispersion cycled 10 times. They also showed that gravitational sedimentation could be overcome with a magnetic field which would be required for any applications to be feasible.

Stébé *et al*. imprinted hard mesoporous silica with magneto-responsivity by using soft colloidal templates formed by magnetic surfactants (Figure 7) [65]. While structuring inorganic material with surfactants is well established [65], this concomitant magnetization is a new concept. Such materials are of fundamental interest as they combine high surface area and pore volume with magnetic responsivity with potential applications in catalysis and separations, as well as for simultaneous MR imaging and drug delivery [66]. The authors used a sol-gel technique to template the silica followed by removal of the surfactant cation by exposing to an atmosphere of trimethylamine with moderate heating. Whereas the previously employed nanoparticulate approaches led to inhomogenities of the final materials [67], this surfactant method led to homogenously distributed magnetic ions evenly distributed in the mesopores. Small-angle X-ray scattering (SAXS) data showed that the structure of the final materials Fe@SiO_2 was preserved with no iron oxide impurities present. SQUID magnetometry indicated that magnetic responsiveness arose from the electronic and molecular spin, associated with the ordering in the resulting architectures with spin transitions occurring due the isolated iron ions being geometrically constrained on the silica walls.

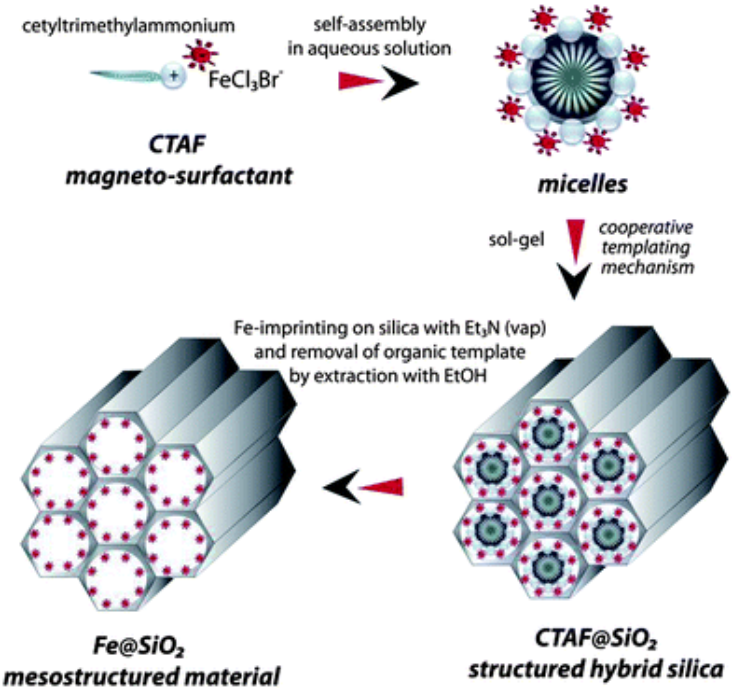


Figure 7: Schematic illustration of the synthetic pathway for magnetic mesoporous silica through a self-assembly mechanism with cetyltrimethylammonium bromotrichloroferrate (CTAF). Reproduced from Ref. [65] with permission from The Royal Society of Chemistry.

.In a later paper the authors used similar templated silica supports combined with solid lipid nanoparticles to catalyze the degradation of methylene blue in aqueous solution by a Fenton-like reaction [68]. The resulting silica matrix degraded the pollutant with twelve time less iron oxide than previously reported. This provides a new way of considering metallosurfactants that had previously always involved the chelation of metal ions.

3. Chelated surfactants – Class 2

The first metallosurfactants were synthesized by Le Moigne *et al.* [69] and utilized a "macrocyclic polar head able to include spherical or quasi-spherical cations and a long paraffinic tail". Since then many different complexing agent-metal ion combinations have been introduced [70-75]. The difference between these compounds and the ionic surfactants mentioned above is simply that they were coordinated with two or more separate sites rather by simple electrostatic interactions. In some cases up to seven donor centers can encapsulate the metal ions, which is particularly important for *in vivo* application (Figure 8) [74]. For example, Gd^{3+} is an ideal element for use as a paramagnetic contrast agent in magnetic resonance tomography (MRT), especially for brain tumor enhancements [76]. However, uncomplexed Gd ions are rather toxic to the body as they interfere with a number of calcium-ion channel dependent processes. By strongly complexing the ions, solubility improves and lethal doses decrease by up to two orders of magnitude, as uptake into tissue is prevented, allowing for renal release [77]. Though magnetic experiments have been carried out on these compounds they have largely been limited to spin-orientation and relaxation studies [74].

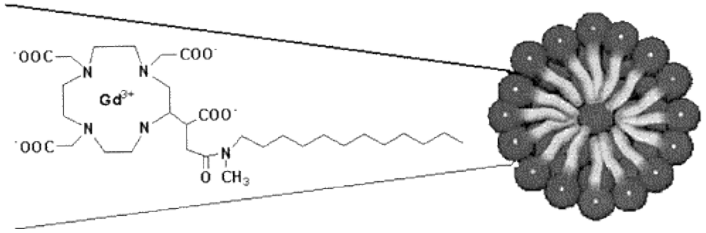


Figure 8: Schematic representation of a micelle formed by 7 donor amphiphilic $[Gd(DOTA\text{-}C_{12})(H_2O)]^-$ complexes [74]. Reprinted with permission from Chem. Rev., 2002, 102 (6), 2303–2345. Copyright 2002 American Chemical Society.

Binnemans *et al*. has also introduced metallolipids [74]. Unlike most surfactants, the phospholipids form bilayers rather than micelles due to packing parameter arguments (rather two fatty chains that cannot efficiently pack into micelles). At higher amphiphile concentrations mesophase formation was observed and liquid crystals were generated thereby earning the compounds the name metallomesegens as well [78]. Such lanthanide containing metallolipids were able to form liquid crystals with large magnetic anisotropy at room temperature, due to large crystal-field perturbation [79]. The systems they investigated were highly viscous, preventing fast switching but the demonstrated that by cooling at rates less than 1 ^{o}C min^{-1} they could achieve good alignment in a magnetic field going from an isotropic liquid to mesophases. At lower concentrations in aqueous solution metallolipid bicelles could also be aligned in a magnetic field. The bicelles were prepared from a mixture of long chain bilayer forming 1,2-dimyristoyl-*sn*-glycero-3-phosphocholine (dimyristoylphosphatidylcholine, DMPC) and short-chain 1,2-dihexanoyl-*sn*-glycero-3-phosphocholine (dihexanoylphosphatidylcholine, DHPC with the bicelle geometry dependent on the molar ratio q = [DMPC]/[DHPC]. The authors reported that when the q ratio was reduced, the bicelle diameter is correspondingly reduced. Below a certain threshold value of the diameter, the bicelles are no longer able to maintain the magnetic alignment and an isotropic solution is observed. When $2 < q < 5$, a magnetically aligned phase is readily formed. Approximate dimensions of disk-like bicelles used in membrane studies are 200 × 40 Å^2.

Windhab *et al*. have since applied magnetic fields as structuring forces on phospholipid-based vesicular systems using chelates covalently bound to lipids with various lanthanide metal ions, as “magnetic handles” attached to the vesicle membrane [80]. They used SANS in magnetic fields up to 8 T to demonstrate the critical lipid domain sizes required for magnetic orientation and alignment to occur. Figure 9 shows the SANS profiles for mixtures of 1-palmitoyl-2-oleoyl-*sn*-glycero-3-phosphocholine (POPC), and 1,2-dimyristoyl-*sn*-glycero-3-phosphoethanolamine-diethylenetriaminepentaacetate (DMPE-DTPA) chelated with Thulium (Tm^{3+}, selected due to large magnetic anisotropy) at a ratio of 4:1:1. The most pronounced effects occurred at lower temperatures (~2.5 ^{o}C) and increasing the magnetic field stepwise from 0 T to 8 T led to a gradual increase in anisotropy of the scattering pattern. Anisotropy was observed below 17 ^{o}C due to lipid demixing and the formation of ordered domains. The change in profile shape was due to an alteration in thickness (5nm to 3.5 nm,

20%) of the membrane parallel to the magnetic field in the case of Tm^{3+} and perpendicular to the field with Dy^{3+}.

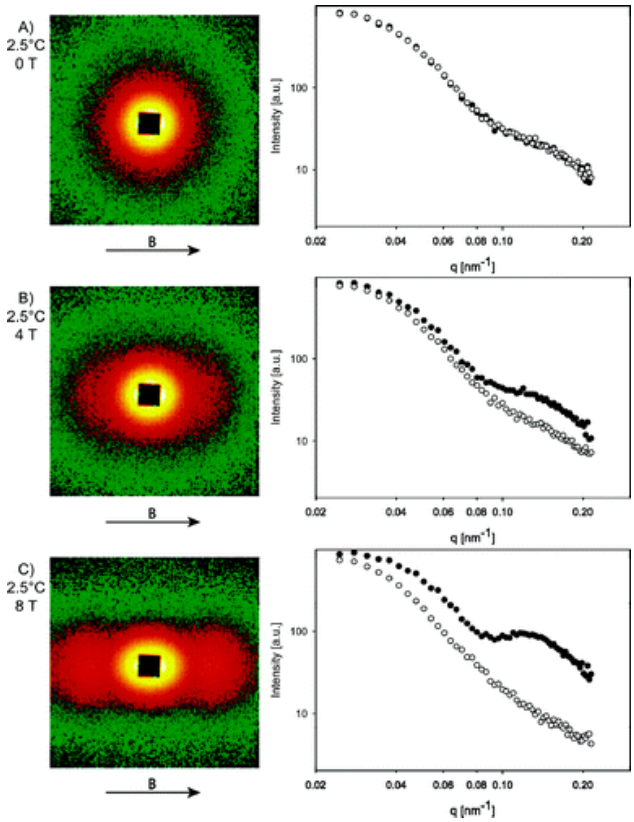


Figure 9: Effect of magnetic field strength on 2D SANS patterns and corresponding sectoral intensity average at 2.5 °C of vesicles consisting of POPC/DMPE-DTPA·Tm. The molar ratio of POPC:DMPE-DTPA:Tm was 4:1:1, and total lipid concentration was 15 mM. Open circles: vertical 15° intensity average. Solid circles: horizontal 15° intensity average. Arrows indicate magnetic field direction [80]. Reprinted with permission from J. Phys. Chem. B, **2010**, 114 (1), 174-186. Copyright 2010 American Chemical Society.

These results demonstrate the importance of domain size and anisotropy effect suggesting that magnetic surfactant micelles may not orientate themselves in a magnetic field but their conjugates (whether with proteins, inorganic material, *etc*.) might.

More recently, Polarz and co-workers developed a surfactant based on a monoalkylated, decyl-modified 1, 4, 7, 10-tetraazacyclododecane-1, 4, 7, 10-tetraacetic acid (C_{10}DOTA) [81] that had been touted as a potentially medically important chelator [82]. The chelator was shown to behave like conventional surfactants. Dynamic light scattering (DLS) showed a hydrodynamic radius of the micelle at D_H=3.6 nm, and lamella phases at higher

concentrations, confirmed by small-angle x-ray scattering (SAXS). Then, the authors selected a Dy^{3+} metal center, due to a high magnetic moment (10.48 μ_B), to coordinate with the surfactant. Coordination caused the solubility to drop to around 0.5 mg mL^{-1} and become pH dependent. Furthermore, dynamic light scattering (DLS) showed small aggregates of a round D_H= 2 nm, assumed to be micelles. On heating, growth of the micelles occurred with structures reaching 210 nm in size and on cooling dumbbell structures could be observed after a couple of days (Figure10). Similar phenomena have been reported before in literature, albeit rarely. The novelty here arises from the magnetic interactions, which the authors conclude, plays a crucial role, as similar effects were not observed for analogous non-magnetic Lu^{3+}-based compounds. Though magnetic studies were not extensive the authors succeeded in demonstrating that, using magnets (< 1T – though fairly large, response was instantaneous), the self-assembled paramagnetic [Dy-C_{10}DOTA] complexes may be manipulated and that self-organization may be driven by long-range magnetic interactions (Figure 10).

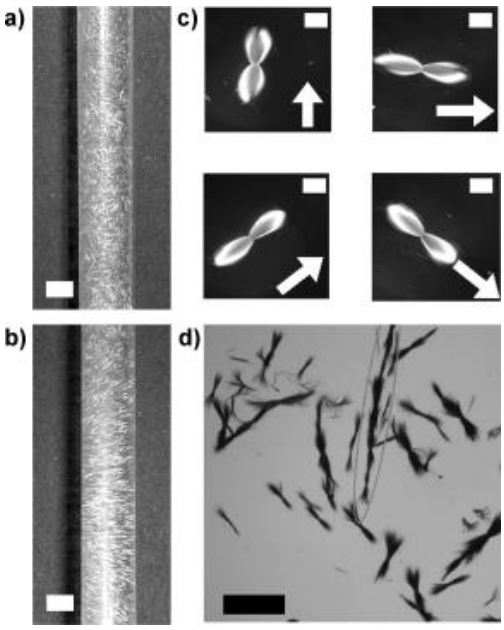


Figure 10: Photographic images of a) randomly oriented [Dy-C_{10}DOTA] tactoids in the absence of a magnetic field. b) Orientation takes places when a field is applied. Scale bar: 2.5 mm. c) Polarization microscopy images of one particle and its alignment in the direction of the magnetic field (indicated by the white arrow) present during the measurement. Scale bar: 100 μm. d) Chain-like tactoid structures, obtained by growth in the presence of a static magnetic field. Scale bar: 0.5 mm [81]. Reprinted with permission from Angew. Chem. Int. Ed., 2013, 52 (51), 13665-13670.

Surprisingly, there are a large number of metal-chelating surfactants for which the magnetic properties have never been studied but would likely exhibit a magnetic response [74, 83]. An especially interesting example includes the iron-chelating microbial surfactant, marinobactin E (M_E), studied by Butler *et al*. [84]. This six-amino-acid peptide amphiphile appended by palmitic acid (C_{16}) shrinks from 4.0 nm to 2.8 nm micelles on coordinating with equimolar amounts of Fe(III) but undergoes a micelle to unilamellar vesicle (~200 nm) transition in the presence of excess Fe(III) (Figure 11).Unfortunately, no magnetic studies were carried out.

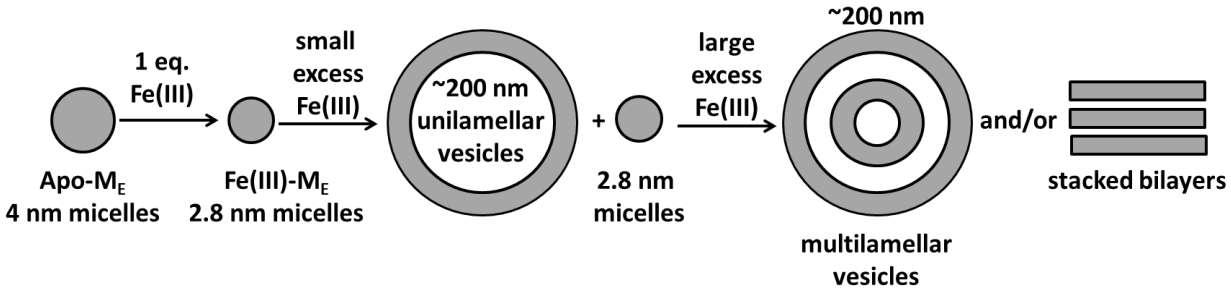


Figure 11: Phase Behavior of M_E as a Function of Fe(III)/M_E Ratio [84]. Redrawn with permission from Langmuir, **2005**, 21 (26), 12109-12114. Copyright 2005 American Chemical Society.

4. Polyoxometalate Surfactants (POMS) – Class 3

So far the review has covered ionic surfactants with metal counterions, however surfactants that contain multivalent *d*- or *f*-block metal ions as an integral part of the surfactant polar headgroup have also been reported. Initially, these surfactants were developed as a class of redox-responsive surfactants that consisted of transition metal oxyanion headgroups linked together by shared oxygen atoms to form clusters called polyoxometalates (POMs). Cronin e*t al*. formed headgroups based on Mn-Anderson clusters functionalized with two alkyl chains forming vesicles in acetonitrile/water mixtures [85]. Since then work in this area has intensified due to potential applications ranging from catalysis and energy storage to medicine and magnetic materials [86]. The use of POMs for obtaining compounds that are magnetically active is well established [87] with many of them being investigated as molecular-based magnets. An interesting example of their use is as spin quibits suitable for the design and implementation of quantum computers. Loss *et al*. proposed tuning the magnetic properties $[PMo_{12}O_{40}(VO)_2]^{q-}$ units electrochemically to provide a method for implementing spin

quibit gates for quantum computers [88]. It is possible that POM based surfactants (POMS) might allow for easy templating routes or the formation of Langmuir-Blodgett films for application realization in data storage *etc*. One potential candidate could be a new Ru-based POMS, which, in 2012, demonstrated reversible redox-responsivity, caused by electrochemical activity converting the Ru-metal centre between non-magnetic low-spin d^6 and magnetic high-spin d^5 configurations [10]. The change in magnetic properties was nicely demonstrated using electron paramagnetic resonance (EPR) but unfortunately no further investigations were reported (Figure 12).

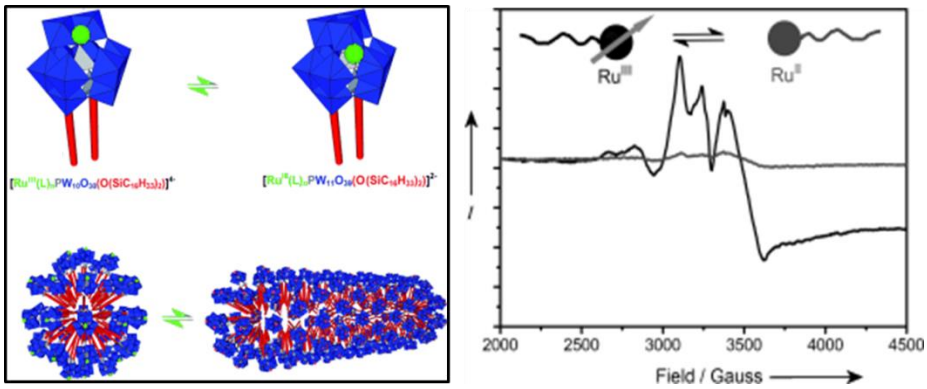


Figure 12: (left) Reversible electrochemical switching of bimetallic Ru-POM surfactants from spherical to rod-like micelles. **(right)** Electrochemical switching of the magnetic properties of the Ru-POMSURF **3 a** investigated by EPR spectroscopy before (black) and after reduction (grey) [10]. Reprinted with permission from Angew. Chem. Int. Ed., **2012**, 51 (24), 5995-5999.

5. Organic-based molecular magnets – Class 4

For many years materials have been developed with a high density of radicals and spin-bearing states which would give rise to ferromagnetic ordering [89, 90]. However, in most cases ferromagnetism was only observed at cryogenic temperatures. In 2004, Zaidi *et al*. reported a new type of polymer, PANiCNQ, produced from polyaniline (PANi) and an acceptor molecule, tetracyanoquinodimethane (TCNQ), which was air stable had a six interacting spins giving rise to a net spin of S=1 per monomer unit [91]. This polymer was ferromagnetic up to its Curie temperature of around 350 K and had an estimated maximum saturation magnetization of 0.1 $JT^{-1}kg^{-1}$. In 2007, Saito *et al*. reported a much smaller 2, 2, 6, 6,-tetramethyl-1-piperidinyloxyl-4-sulfate (TEMPO-

OSO_3) anion with S- ½ radical spin, which formed an ionic liquid when combined various imidazlium cations (Figure 13) [92].

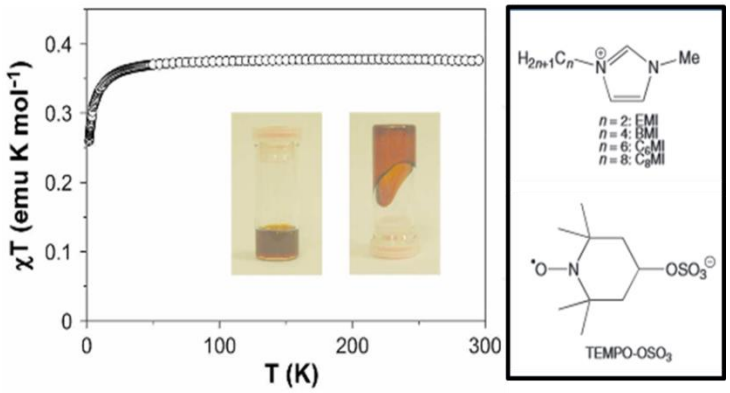


Figure 13: (left) Temperature dependence of the product of static susceptibility and temperature (χT) for [C4MI][TEMPO-OSO3] in an applied field of 1 kOe on heating process. The inset is the photographs of [C4MI][TEMPO-OSO3]; **(right)** Structure of [TEMPO-OSO3] anion and tyrpical imidazolium cation [92]. Reprinted with permission from Chem. Lett., 2007, 36 (9), 1096-1097.

With effective magnetic moments around 1.70 μ_B at 70 ^oC the compounds represented the first genuine organic paramagnetic ionic liquids. Just like the first MILSs that extended the cation chain length of metal containing ILs to induce surface-activity, it might be expected that the same approach could be used here to generate the first metal-free magnetic surfactants with potential in templating materials suitable for spin-tronics *etc*.

6. Non-identical Magnetic Centres

So far only ensembles of identical molecules have been investigated, be they micelles, liquid crystal phases, or adsorbed monolayers. However, if some kind of magnetic exchange interaction does occur between metal centres (below the Curie temperature), then investigating mixed surfactant systems with non-identical magnetic ions would be especially interesting. The role of surfactant in controlling molecular packing should have a particularly useful knock-on effect of altering the intermolecular magnetic interactions and overall behavior of the system in a way not possible via crystallization or by using conventional (non-self-aggregating) molecular

magnets [93]. In addition gemini surfactants may be considered as novel dimeric molecular magnets with the ultimate conclusion being magnetic polymers similar to those introduced above.

7. Conclusions

This review has discussed the synthesis of different classes of magnetic surfactants and proposed a potential new class ready to be studied [90, 91]. Various proof of principle experiments have been highlighted that have already been demonstrated in areas of protein separations [44, 46], water treatment [62] and environmental clean-up [37]. Furthermore, the concept that these complexes may be considered as novel molecular magnets has been highlighted [10]. The review has also pointed out limitations, especially where current understanding is lacking and where future investigations are required. The field is rich, wide open and exciting horizons remain to be explored.

References

Certain references have been selected as particularly significant: [14], [20], [30], [44], [65], [70], [74], [80], [81], and [90].

1) Rosen J, Surfactants and Interfacial Phenomena: Edition 3, Wiley, **2004.**
2) Otzen, D, Protein-surfactant interactions: a tale of many states, Biochim. Biophys. Acta, **2011**, 1814 (5) 562-591.
3) Surfactants: Chemistry, Interfacial Properties, Applications, Ed. Fainerman VB, Mobius D, Miller R, Elsever, Amsterdam, **2001**.
4) Nardello-Rataj VR, Caron L, Borde CD, Aubry JM, Oxidation in Three-Liquid-Phase Microemulsion Systems Using Balanced Catalytic Surfactants, J. Am. Chem. Soc., **2008**, 130 (45), 14914–14915.
5) Brown P, Butts CP, Eastoe J, Stimuli-responsive surfactants, Soft Matter, **2013**, 9, 2365-2374.
6) Liu Y, Jessop PG, Cunningham M, Eckert CA, Liotta CL, Switchable Surfactants, Science, **2006**, 313, 958–960.

7) Liu X, Abbott NL, Spatial and temporal control of surfactant systems, J. Colloid Interface Sci., **2009**, 339 (1), 1–18.

8) Ku TH, Chien MP, Thompson MP, Sinkovits RS, Olson NH, Baker TS, Gianneschi NC, Controlling and Switching the Morphology of Micellar Nanoparticles with Enzymes, J. Am. Chem. Soc., **2011**, 133, 8392–8395.

9) Saji T, Hoshino K, Aoyagui S, Reversible formation and disruption of micelles by control of the redox state of the surfactant, J. Chem. Soc., Chem. Commun., **1985**, 865–866.

10) Landsmann S, Wessig M, Schmid M, Colfen H, Polarz S, Smart Inorganic Surfactants: more than Surface Tension, Angew. Chem. Int. Ed., **2012**, 51 (24), 5995-5999.

11) Saji T, Hoshino K, Aoyagui S, Reversible formation and disruption of micelles by control of the redox state of the head group, J. Am. Chem. Soc., **1985**, 107 (24), 6865–6868

12) Griffiths PC, Fallis IA, Chuenprattom T, Watanesk R, Metallosurfactants: Interfaces and micelles, Adv. Coll. Int. Sci., **2006**, 122 (1-3), 107-117.

13) Brown P, Butts CP, Eastoe J, Hernandez EP, de Araujo Machado FL, de Oliveira RJ, Dicationic magnetic ionic liquids with tunable heteroanion, Chem. Commun., **2013**, 49, 2765-2767.

14) Brown P, Bushmelev A, Butts CP, Cheng J, Eastoe J, Grillo I, Heenan RK, Schmidt AM, Magnetic Control over Liquid Surface Properties with Responsive Surfactants, Angew. Chem. Int. Ed., **2012**, 51 (10), 2414-2416.

15) Brown P, Bushmelev A, Butts CP, Eloi JC, Grillo I, Baker PJ, Schmidt AM, Eastoe J., Properties of New Magnetic Surfactants, Langmuir, **2013**, 29 (10), 3246-3251.

16) Welton T, Room-Temperature Ionic Liquids. Solvents for Synthesis and Catalysis, Chem. Rev., 1999, 99 (8), 2071-2084.

17) Lipsztajn M, Osteryoung RA, Electrochemistry in neutral ambient-temperature ionic liquids. 1. Studies of iron(III), neodynium(III), and lithium(I), Inorg. Chem. 1985, *24*, 716-719.

18) Bolkan SA, Yoke JT, Room temperature fused salts based on copper(I) chloride-1-methyl-3-ethylimidazolium chloride mixtures. 1. Physical properties, J. Chem. Eng. Data 1986, *31*, 194-197.

19) García-Saiz, A.; Migowski, P.; Vallcorba, O.; Junquera, J.; Blanco, J. A.; González, J. A.; Fernández-Díaz, M. T.; Rius, J.; Dupont, J.; Fernández, J. R.; de Pedro, I. Chem. Eur. J. **2014**, 20, 1

20) Hayashi S, Hamaguchi H, Discovery of a Magnetic Ionic Liquids [bmim]$FeCl_4$, Chem. Lett. 2004, *33*, 1590-1591.

21) De Pedro I, Rojas DP, Albo J, Luis P, Irabien A, Blanco AJ, Rodriguez Fernandez J, Long-range magnetic ordering in magnetic ionic liquid: Emim[$FeCl_4$], J. Phys.: Condens. Matter, **2010**, 22, 296006.

22) del Sesto R E, McCleskey T M, Burrell A K, Baker G A, Thompsom J D, Scott B L, Wilkes J S, Williams P, Chem. Commun., **2008**, 447-449.

23) Genc S, Derin B, Synthesis and rheology of ferrofluids: a review, Curr. Opin. Chem. Eng., **2014**, 3, 118-124.

24) Santos E, Albo J, Irabien A, Magnetic ionic liquids: synthesis, properties and applications, RSC Adv., **2014**, 4, 40008-40018.

25) Yuan Y, Lee TR, Surface Science Techniques, Chpt 1, Ed., Bracco G, Holst B, Springer, Berlin, **2013**

26) Rosenweig RE, Ferrohydrodynamics, Dover, New York, **1998**.

27) Degen P, Zwar E, Paulus M, Rehage H, About the role of surfactants on the magnetic control over liquid interfaces, Langmuir, **2014**, 30 (39) 11563-11566.

28) Cho Y, Park H, Choi W, Novel complexation between ferric ions and nonionic surfactants (Brij) and its visible light activity for CCL4 degredation in aqueous micellar solutions, J. Photochem. Photobiol. A: Chem., **2004**, 165 (1-3), 43-50.

29) Rodríguez JR, González-Pérez A, Del Castillo JL, Czapkiewicz J, Thermodynamics of Micellization of Alkyldimethylbenzylammonium Chlorides in Aqueous Solutions, *J. Coll. Int. Sci.* **2002**, *250 (2)*, 438-443.

30) Brown P, Butts CP, Eastoe J, Glatzel S, Grillo I, Hall SH, Rogers S, Trickett K, Microemulsions as tunable nanomagnets, *Soft Matter* **2012**, 8, 11609-11612.

31) Wang Z, Holm C, Structure and magnetic properties of polydisperse ferrofluids: A molecular dynamics study, Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys., **2003**, 68, 041401.

32) Gatteschi D, Fittipaldi M, Sangregorio C, Sorace L, Exploring the No-Man's Land between Molecuar Nanomagnets and Magnetic Nanopartilces, Angew. Chem., Int. Ed., **2012**, 51, 4792–4800.

33) Klee A, Prevost S,Kunz W, Schweins R, Kiefer K, Gradzielski M, Magnetic microemulsions based on magnetic ionic liquids, Phys. Chem. Chem. Phys., **2012**, 14 *(*44), 15355-15360.

34) Brown P, Wasbrough MJ, Gurkan BE, Hatton TA, CO_2-Responsive Microemulsions Based on Reactive Ionic Liquids, Langmuir, **2014**, 30 (15), 4267-4272.

35) Klier J, Tucker CJ, Kalantar TH, Green DP, Properties and Applications of Microemulsions, Adv. Mater., **2000**, 12, 1751–1757.

36) Kaiser A, Liu T, Richtering W, Schmidt AM, Magnetic Capsules and Pickering Emulsions Stabilized by Core-Shell Particles, Langmuir, **2009**, 25 (13), 7335–7341.

37) Brown P, Butts CP, Cheng J, Eastoe J, Russell CA, Smith GN, Magnetic Emulsions with responsive surfactants, Soft Matter, **2012**, 8, 7545-7546.

38) Murphy RJ, Treatment fluids comprising magnetic surfactants and methods relating thereto, US 20140076552 A1, WO 2014043191.

39) Lee IS, Lee N, Park J, Kim BH, Yi YW, Kim T, Kim TK, Lee IH, Paik SR, Hyeon T, Ni/NiO Core/Shell Nanoparticles for Selective Binding and Magnetic Separation of Histidine-Tagged Proteins, J. Am. Chem. Soc. **2006**, 128, 10658–10659.

40) Dobson J, Gene therapy progress and prospects: magnetic nanoparticle-based gene delivery, Gene Therapy, **2006**, 13, 283-287.

41) McBain SC, Yiu H, Dobson J, Magnetic nanoparticles for gene and drug delivery, Int. J. Nanomed., **2008**, 3, 169-180.

42) Mykhaylyk O, Vlaskou D, Tresilwised N, Pithayanukul P, Moller W, Plank C, Magnetic nanoparticle formulatios for DNA and siRNA delivery, J. Magn. Magn. Mater., **2007**, 311, 275-281.

43) Tartaj P, Morales MP, González-Carreño T, Veintemillas-Verdaguer S, Serna CJ, Advances in magnetic nanoparticles for biotechnology applications, *J*. Magn. Magn. Mater., **2005**, 290–291 *(1),* 28–34.

44) Brown P, Khan AM Armstrong JPK, Perriman AW, Butts CP, Eastoe J, Magnetizing DNA and Proteins Using Responsive Surfactants, *Adv. Mat.*, **2012**, 24 (46), 6244-6247.

45) Xu L, Feng L, Hao J, Dong S, Controlling the Capture and Release of DNA with a Dual-Responsive Cationic Surfactant, *ACS Appl. Mater. Interfaces*, **2015**, DOI: 10.1021/acsami.5b01514.

46) Brown P, Bromberg L, Rial-Hermida MI, Wasbrough MJ, Lorenzo CA, Hatton TA, New magnetic metallosurfactants and polymers based on gadolinium counterions for applications in biotechnology, **2015**, Submitted.

47) Mori K, Emoto M, Inaba M, Fetuin-A: a multifunctional protein, *Recent Pat. Endocr. Metab. Immune Drug Discov.* **2011**, 5, 124-146.

48) Bedford EE, Spadavecchia J, Pradier CM, Gu FX, Surface plasmon resonance biosensors incorporating gold nanoparticles, *Macromol. Biosci.*, **2012**, 12, 724-739.

49) Shukla R, Bansal V, Chaudhary M, Basu A, Bhonde RR, Sastry M, Biocompatibility of gold nanoparticles and their endocytotic fate inside the cellular compartment: a microscopic overview, *Langmuir*, **2005**, 21, 10644-10654.

50) Alric C, Taleb J, Le Duc G, Mandon C, Billotey C, Le Meur-Herland A, Brochard T, Vocanson F, Janier M, Perriat P, Roux S, Tillement O, Gadolinium Chelate Coated Gold Nanoparticles As Contrast Agents for Both X-ray Computed Tomography and Magnetic Resonance Imaging, *J. Am. Chem. Soc.*, **2008**, 130, 5908-5915.

51) Xu L, Feng L, Dong S, Hao J, Magnetic controlling of migration of DNA and proteins using one-step modified gold nanoparticles, *Chem. Commun.*, **2015**, DOI: 10.1039/C5CC01738F.

52) Clark KD, Nacham O, Yu H, Li T, Yamsek MM, Ronning DR, Anderson JL, Extraction of DNA by Magnetic Ionic Liquids: Tunable Solvents for Rapid and Selective DNA Analysis, Anal. Chem., **2015**, 87 (3), 1552-1559.

53) D'Anna F, Noto R, Di- and Tricationic Organic salts: An Overview of Their Properties and Applications, Eur. J. Org. Chem., **2014**, 2014, 4201-4223.

54) Cote LJ, Kim J, Zhang Z, Sun C, Huang J, Tunable assembly of graphene oxide surfactant sheets: wrinkles, overlaps and impacts on thin film properties, Soft Matter, **2010**, 6, 6096-6101.

55) Cote LJ, Kim J, Tung VC, Luo J, Kim F, Huang J, Graphene oxide as surfactant sheets, Pure Appl. Chem., **2011**, 83 (1), 95-110.

56) Losurdo M.; Bergmair, I.; Dastmalchi, B.; Kim, T.-H.; Giangregroio, M. M.; Jiao, W.; Bianco, G. V.; Brown, AS, Hingerl K, Bruno G, Graphene as an Electron Shuttle for Silver Deoxidation: Removing a Key Barrier to Plasmonics and Metamaterials for SERS in the Visible, Adv. Funct. Mater., **2014**, 24, 1864– 1878.

57) Kim H, Park KY, Hong J, Kang K, All-graphene-battery: bridging the gap between supercapacitors and lithium ion batteries, Scientific Reports, **2014**, 4, 5278.

58) Gao Y, Li Y, Zhang L, Huang G, Hu J, Shah SM, Su X, Adsorption and Removal of Tetracycline Antibiotics from Aqueous Solution by Graphene Oxide, J. Coll. Int. Sci., **2012**, 368, 540–546.

59) Zhao G, Li J, Ren X, Chen C, Wang X, Few-Layered Graphene Oxide Nanosheets As Super Sorbents for Heavy Metal Ion Pollution Management, Environ. Sci. Technol., **2011**, 45, 10454–10462.

60) Deng JH, Zhang XR, Zeng GM, Gong JL, Niu QY, Liang J, Simultaneous Removal of Cd(II) and Ionic Dyes from Aqueous Solution using Magnetic Graphene Oxide Nanocomposite as an Adsorbent, Chem. Eng. J., **2013**, 226, 189–200.

61) Fu Y, Wang J, Liu Q, Zeng H, Water-Dispersible Magnetic Nanoparticle-Graphene Oxide Composites for Selenium Removal, Carbon, **2014**, 77, 710–721.

62) McCoy TM, Brown P, Eastoe J, Tabor RF, Noncovalent Magnetic Control and Reversible Recovery of Graphene Oxide Using Iron Oxide and Magnetic Surfactants, ACS Appl. Mater. Interfaces, **2015**, 7 (3), 2124-2133.

63) Smith, GN, Eastoe J, Magnetically-responsive electrophoretic silica organosols, J. Coll. Int. Sci., **2014**, 426, 252-255.

64) Comiskey B, Albert JD, Yoshizawa H, Jacobson J, An electrophoretic ink for all-printed reflective electronic displays, Nature, **1998**, 394, 253–255.

65) Kim S, Bellouard C, Pasc A, Lamouroux E, Blin JL, Carteret C, Fort Y, Emo M, Durand P, Stébé MJ, Nanoparticle-free magnetic mesoporous silica with magneto-responsive surfactants, J. Mat. Chem. C, **2013**, 1 (42), 6930-6934.

66) Tarn D, Ashley CE, Xue M, Carnes EC, Zink JI, Brinker CJ, Mesoporous silica nanoparticle nanocarriers: biofunctionality and biocompatibility, Acc. Chem. Res., **2013**, 46 (3), 792-801.

67) Carta D, Bullita S, Casula MF, Casu A, Falqui A, Corrias A, Cubic Mesoporous Silica (SBA-16) Prepared Using Butanol as the Co-Surfactant: A General Matrix for the Preparation of FeCo-SiO2Nanocomposites, ChemPlusChem, 2013, 78, 364-374.

68) Kim S, Durand P, Roques-Carmes T, Eastoe J, Pasc A, Metallo-Solid Lipid Nanoparticles as Colloidal Tools for Meso-Macroporous Supported Catalysts, Langmuir, 2015, 31 (5), 1842-1849.

69) Le Moigne J, Simon J, A new type of surfactants. The annelids. Characterization of organized metal ion assemblies obtained by cationic complexation at the micelle subsurface, J. Phys. Chem., **1980**, 84 (2), 170-177.

70) Bruce DW, Dunmur DA, Maitlis PM, Watkins JM, Tiddy GJT, The synthesis and lyotropic phase behavior of some aquatetra(cyano)-dodecylaminoferrate(II) complexes, Liq. Cryst., **1992**, 11, 127–133.

71) Bruce DW, Denby IR, Tiddy GJT, Watkins JM, Synthesis and properties of surfactant complexes of cobalt (III) and chromium (III), J. Mater. Chem., **1993**, 3, 911–916.

72) Neve F, Ghedini M, Demunno G, Levelut AM, Ionic Aphiphilic Metallomesogens, Chem. Mater., **1995**, 7 (4), 688–693.

73) Zhu SS, Swager TM, Lyotropic polymorphism in oxovanadium complexes, Adv. Mater., **1995**, 7 (3), 280–283.

74) Binnemans K, Görller-Walrand C, Lanthanide-Containing Liquid Crystals and Surfactants, Chem. Rev., **2002**, 102 (6), 2303–2345.

75) Polarz S, Landsmann S, Klaiber A, Hybrid Surfactant Systems with Inorganic Constituents, Angew. Chem. Int. Ed., 2014, 53 (4), 946-954.

76) Zhou Z, Lu ZR, Gadolinium-Based Contrast Agents for MR Cancer Imaging. Wiley Interdisciplinary Reviews. Nanomedicine and Nanobiotechnology, **2013**, *5*(1), 1–18.

77) Penfield JG, Reilly Jr. RF, What nephrologists need to know about gadolinium, Nat. Clin. Pract. Nephrol., **2007**, 3 (12), 654–668.

78) Metallomesogens, synthesis, properties, and applications, Ed. Serrano JL,VCH, **2006**.

79) Vold RR, Prosser RS, Magnetically orientated phospholipid bilayered micelles for structural studies of polypeptides. Does the ideal bicelle exist?, J. Magn. Reson., Series B, **1996**, 113 (3), 267-271.

80) Beck P, Liebi M, Kohlbrecher J, Ishikawa T, Ruegger H, Zepik H, Fischer P, Walde P, Windhab E, Magnetic Field Alignable Domains in Phospholipid Vesicle Membranes Containing Lanthanides, J. Phys. Chem. B, **2010**, 114 (1), 174-186.

81) Polarz S, Bahrle C, Landsmann S, Klaiber A, Panoscopic Structures by Hierarchical Cascade Self-Assembly of Inorganic Surfactants with Magnetic Heads Containing Dysprosium Ions, Angew. Chem. Int. Ed., **2013**, 52 (51), 13665-13670.

82) Jagadish B, Brickert-Albrecht GL, Nichol GS, Mash EA, Raghunand N, On the synthesis of 1,4,7-tri(tert-butoxycarbonylmethyl)-1,4,7,10-tetracyclododecane, Tetrahedron Lett., **2007**, 48, 8052-8055.

83) Griffiths PC, Fallis IA, Willock DJ, Paul A,Barrie CL, Griffiths PM, Williams GM,King SM, Heenan RK, Goergl R, The Structure of etallomicelles, Chem. Eur. J., **2004**, 10 (8), 2022-2028.

84) Owen T, Pynn R, Martinez JS, Butler A, Micelle-to-vesicle Transition of an Iron-Chelating Microbial Surfactant, Marinobactin E, Langmuir, **2005**, 21 (26), 12109-12114.

85) Zhang J, Song YF, Cronin L, Liu T, Self-Assembly of Organic-Inorganic Hybrid Amphiphilic Surfactants with Large Polyoxometalates as Polar Head Groups, J. Am. Chem. Soc., **2008**, 130 (44), 14408–14409.

86) Giner-Casares JJ, Brezesinski G, Mohwald H, Landsmann S, Polarz S, Polyoxometalate Surfactants as Unique Molecules for Interfacial Self-Assembly, J. Phys. Chem. Lett., **2012**, 3 (3), 322-326.

87) Coronada E, Gomez-Garcia CJ, Polyoxometalate-Based Molecular Materials, Chem. Re., 1998, 98 (1), 273-296.

88) Lehmann J, Gaita-Arino A Coronada E, Loss D, Spin quibits with electrically gated poloxometallate molecules, Nat. Nanotech., **2007**, 2, 312-317.

89) Miller JS, Calabrese JC, Rommelmann H, Chittipeddi SR, Zhang JH, Reiff WM, Epstein AJ, Ferromagnetic behavior of [Fe(C5Me5)2]+.bul.[TCNE]-.bul.. Structural and magnetic characterization of decamethylferrocenium tetracyanoethenide, [Fe(C5Me5)2]+.bul.[TCNE]-.bul..cntdot.MeCN and decamethylferrocenium pentacyanopropenide, [Fe(C5Me5)2]+.bul.[C3(CN)5]-, J. Am. Che. Soc., **1987**, 109 (3), 769-781.

90) Wudl F, Thompson JD, Buckminsterfullerene C_{60} and organic ferromagnetism, J. Phys. Chem. Solids, **1992**, 53 (11) 1449-1455.

91) Zaidi NA, Giblin SR, Terry I, Monkman AP, Room temperature magnetic order in an organic magnet derived from polyaniline, Polymer, **2004**, 45 (16), 5683-5689.

92) Yoshida Y, Tanaka H, Saito G, Organic Paramagnetic Ionic Liquid Based on Anion Containing 2,2,6,6-Tetramethyl-1-piperidinyloxyl Radical Moiety, Chem. Lett., **2007**, 36 (9), 1096-1097.

93) Feltham HLC, Brooker S, Review of purely 4f and mixed-metal nd-4f single molecular magnets containing only one lanthanide ion, Coord. Chem. Rev., **2014**, 276, 1-33.